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Creation of nanoparticles and surface nanostructures of alumina by hot water treatment

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Abstract. In this report, we present a detailed study of the formation of alumina nanostructures at the surface of aluminium plate by hot water treatment (HWT) at various temperatures. The nanostructures were studied by scanning electron microscopy. The superhydrophilic property of the treated surface was revealed and its stability was investigated. It was shown that HWT could be used also for synthesis of the aqueous suspensions of alumina nanoparticles. It is proposed that the method can be applied for production of surface nanostructures and nanoparticles of various metal oxides.

1. Introduction

Nanomaterials have numerous applications in various areas, such as catalysis [1], photonics [2], molecular computing [3], energy storage [4,5], fuel cells [6,7], sensing [8-10], and nanomedicine [11-15]. This is due to increased reactivity compared to their micro-sized counterparts, since nanoscale materials have extremely high value of surface-to-volume ratio; therefore, their properties are no longer dominated by the bulk of the material but by the surface atoms.

There are several ways to obtain nanoscale materials: electrochemical synthesis [16-18], chemical vapour deposition [19], molecular beam epitaxy [19,20], pulsed laser ablation [21,22], and pyrolysis of volatile precursors [23-25]. Although these methods allowed producing excellent nanostructured materials of various geometry and complexity, they have their inherent limitations, such as complex and expensive equipment, toxic precursors, and scaling problems.

Metal oxide nanostructures (MONSTRs) and nanoparticles (MONPs) produced by treatment of the metal surface demonstrate unique physical and chemical properties. Recently, MONSTRs have been used in electronic and optical devices [26,27] and sensitive devices of an evidence-based concept [26,28]. However, their synthesis methods have several obstacles that limit their large-scale production.

The growth of hydrous oxide films on the surface of electropolished aluminium in hot water with temperature ranged from 50 to 70°C was discovered more than forty years ago [29]. This effect was applied for durable adhesive bonding [30] and for production of superamphiophobic aluminium alloy surface with nanoscale roughness [31].

Recently, it has been demonstrated that a simple Hot Water Treatment (HWT) process allowed producing MONSTRs on the surface of various metals, their compounds and alloys by a one-step, scalable, low-cost, and eco-friendly process [32]. The HWT process involves immersing the metal piece in hot deionized water without any chemical additives, such as a metal salt and a reducing or

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oxidizing agent. This method already was used for producing of copper (II) oxide nanoleaf structures on Cu sheets for optical photoconductive devices [26].

The boiling water was used to make the aluminium surfaces hydrophilic through the creation of nanostructures [33]. Water treatment of laser-ablated aluminium allowed making it superhydrophilic [33]. The surfaces with changed wettability are used in wide range of applications and industries, for example, in biomedical area as substrates for controlling protein adsorption [34,35], cell interaction [36], and bacterial growth [37,38].

It is seen that HWT is the new promising eco-friendly method for producing MONSTRs of the most metals in the periodic table. But, to date there are no systematic studies of MONSTRs formation. In this report, we present the detail study of formation of superhydrophilic alumina nanostructures and nanoparticles by HWT at various temperatures and treatment durations.

2. Experimental

Aluminium compound plates (Al 97%, Cu 1.2%, Fe 0.7%, Mn 0.3%) with 0.5 mm thickness and 10x10 mm^2 size were used. Just before HWT, the native oxide layer and organic contaminations were removed by ultrafine sandpaper and the sample was cleaned by ultra-sonication in acetone and isopropanol for 5 min each.

Treatment by hot deionized water was done at 60-95°C during 2-30 min. Treatment by boiling water was done for 30 min only. The water volume was always 50 ml. The samples were extracted from the water after HWT and dried by airflow.

Wettability of the treated surfaces was characterized by water droplet contact angle obtained by sessile drop technique. The measurements were carried out after careful sample drying with compressed air. The water droplet of 10 µl volume was placed on the surface and its profile was recorded by high resolution camera FASTCAM Mini UX100 (Photron, Germany).

The imaging of the plate surface morphology was performed by scanning electron microscopy (SEM) using dual-beam workstation Auriga CrossBeam (Carl Zeiss, Germany) operated at accelerating voltage of 3 kV and beam current about 100 pA. The secondary electron detection mode with resolution down to 2 nm was used.

The thickness of alumina nanostructure was measured by SEM imaging of the cross-sections produced by focused Ga+ ion beam (FIB) operated at accelerating voltage of 30 kV and beam current of 1 nA. The elemental composition was measured by means of energy-dispersive X-ray spectroscopy (EDS) using X-Max N detector and analysed by Aztec software (Oxford Instruments, UK).

The shape and sizes of nanoparticles were revealed by analysis of SEM images. The samples for SEM imaging were prepared by vacuum freeze drying (lyophilization) of the water suspension drop on the Si/SiO_2 substrate by freeze dryer Alpha 2-4 LSC (Martin Christ, Germany).

3. Results and discussion

3.1. Nanostructure morphology

The study of nanostructures formed at various durations of HWT at fixed water temperature (80°C) allowed us to reveal three stages of nano-sheets formation. At the end of the first stage, for HWT duration below 8 min, the metal surface was covered by isolated nanowires (Fig. 1a,b). At the end of the second stage, for HWT duration about 16 min, the surface was completely covered by three-dimensional maze-like nanostructure consisting of nanowires (Fig. 1c). At the last stage, for HWT duration above 30 min, the nano-sheets mostly oriented normally to the plate surface with average thickness about 10 nm formed over the maze structure (Fig. 1d).

The element analysis of the aluminium plate surface layer was performed before and after HWT. It was obtained that the nanostructured layer appeared after HWT consisted of alumina nano-sheets.

Investigation of the obtained nanostructured layers allowed revealing significant increase in nano-sheets concentration with water temperature (Fig. 2).

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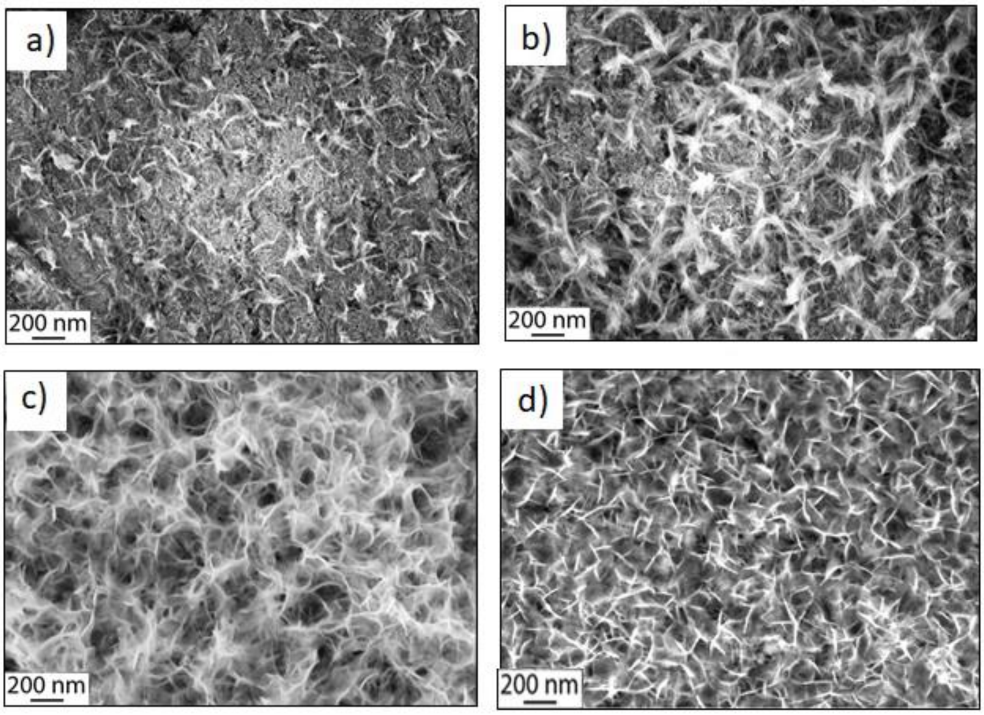

Figure 1. SEM images of the surface of aluminium plate after HWT at 80°C for various treatment durations, min: (a) 4, (b) 8, (c) 16, (d) 30.

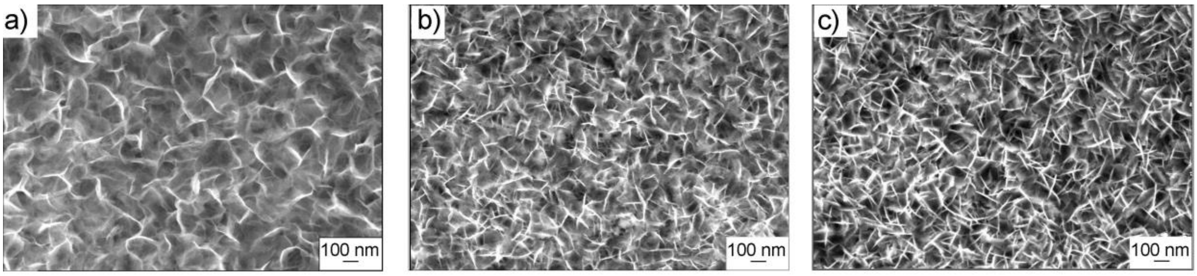

Figure 2. SEM images of aluminium oxide nanostructures on surface plates after HWT during 30 minutes at various temperatures, °C: (a) 70, (b) 80, (c) 95.

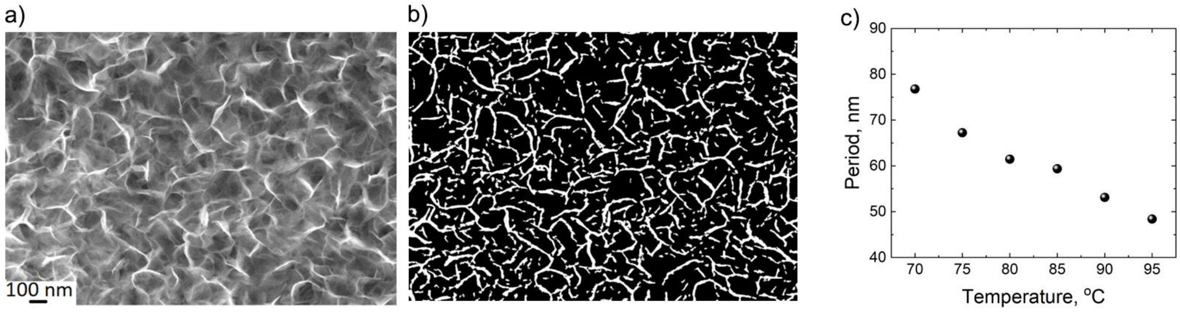

Figure 3. SEM image of alumina nanostructure produced by HWT at 70°C for 30 min: (a) original and (b) binarized. (c) Temperature dependence of the average effective period of the nanostructure obtained after HWT during 30 min.

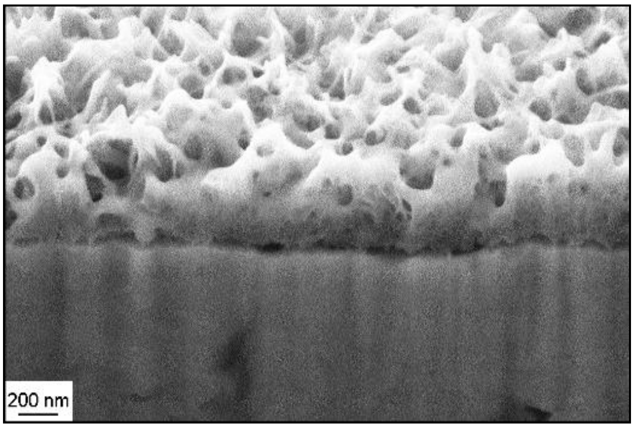

Figure 4. Cross-section of surface nanostructured layer by ion beam.

For quantitative characterization of the effect, we treated the SEM images. The obtained grayscale images were binarised by local adaptive binarisation function (Fig. 3a) with subsequent application of the skeletisation function (Fig. 3b). The obtained skeleton corresponds to the top edges of the nano-sheets. The average period of nanostructure was calculated as a ratio of surface area covered by it to the total length of the skeleton segments. It was obtained that the average effective period of the nanostructure decreased monotonously with water temperature from 76 to 48 nm (Fig. 3c).

The thickness of alumina nanostructured layer was measured at cross-sections produced by FIB (Fig. 4). It was revealed that the layer thickness was nonuniform over the plate surface and the difference could reach 100 nm. It can be attributed to the islet character of nanostructure formation. Places, where isolated nanowires started appearing, had a thicker alumina layer. Such nonuniformity did not allow revealing the temperature dependence of the thickness of nanostructured layer. For HWT at temperatures from 70 to 95°C during 30 min, the layer thickness varied between 350 and 550 nm.

3.2 Change in wettability

It was revealed that appearance of alumina nanostructure led to significant change in the surface wettability. The contact angle of untreated plate surface was about 69°. It was shown that HWT of plate during 30 min at temperature in the range from 70 to 95°C led to appearance of superhydrophilic

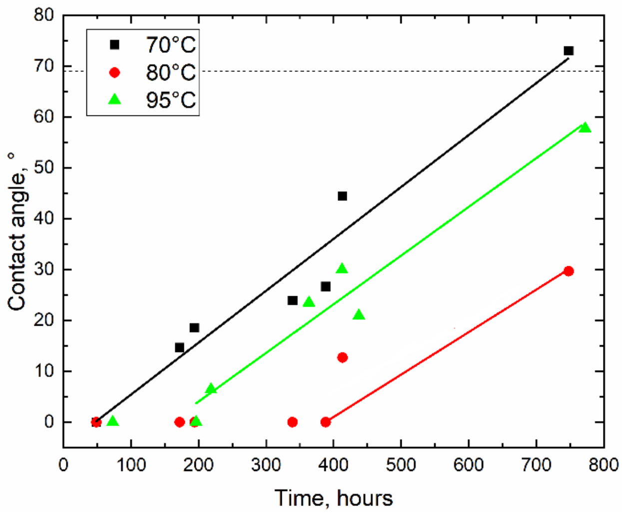

Figure 5. The time dependence of contact angle of alumina nanostructured surface after HWT at different temperatures during 30 min.

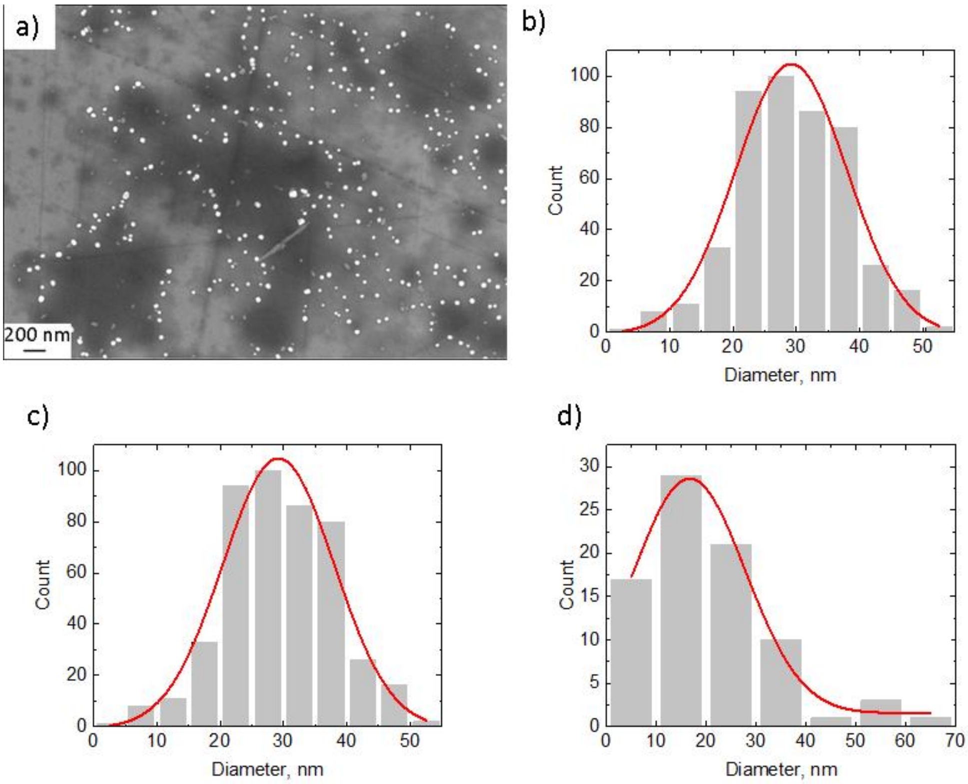

Figure 6. (a) SEM image of alumina nanoparticles obtained as a result of HWT at 80°C. The size distributions of nanoparticles produced at different temperatures, °C: (b) 70, (c) 80, and (d) 95.

property with wetting angle close to zero. The superhydrophilic state remained for about 400 hours after HWT at 80°C and then slowly increased to the initial value. The lifetime increased with the temperature. Nevertheless, the lifetime after HWT at 95°C was essentially shorter. This fact can be attributed to the influence of cavitation caused by boiling near the surface of aluminium plate (Fig. 5).

3.3 Nanoparticles

HWT leads also to appearance of the water suspension of nanoparticles. For SEM visualization of the nanoparticle morphology, the drop of suspension was dried on the Si/SiO_2 substrate (Fig. 6a). It is clearly seen that the synthesized nanoparticles possess mostly spherical shape. These results are in good agreement with those previously reported [39].

The size distributions of the nanoparticles were obtained by analysis of the SEM images (Fig. 6a) using the Image J program. The nanoparticle size distributions are shown in Figure 6b-d. The average sizes of nanoparticles were 29±18 nm for 70°C, 41 ± 18 nm for 80°C, and 17 ± 22 nm for 95°C. So, we can conclude that the temperature does not affect nanoparticle size significantly.

Along with the spherical nanoparticles, the rare isolated nano-filaments with typical width about 25 nm and length above 1 μm were obtained (Fig. 7a). Moreover, the self-assembled bundles of nano-filaments were found (Fig. 7b). The similar shapes were produced by HWT of the aqueous suspensions of CuO nanoparticles produced by laser ablation in water [40].

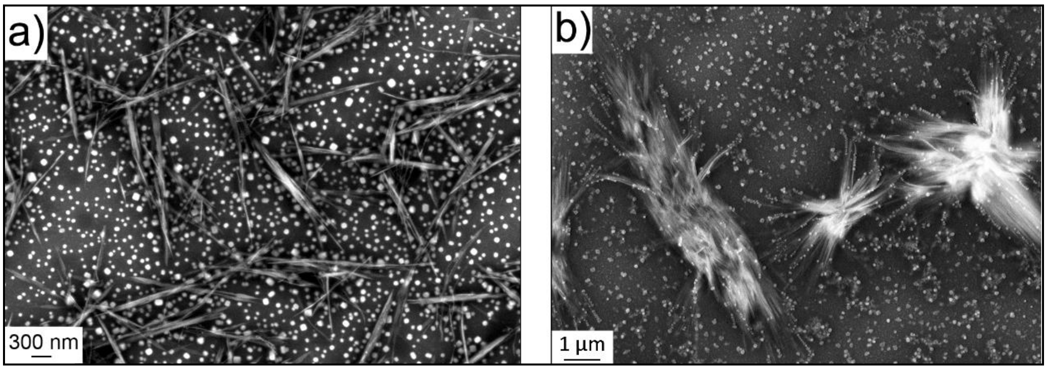

Figure 7. SEM images of Al_2O_3 nano-filaments: (a) individual, (b) bundles.

4. Conclusion

In this work, we have studied the appearance of alumina nanostructures and nanoparticles as a result of hot water treatment of aluminium plate for various water temperatures and treatment times. Three stages of nanostructure formation were revealed. At the beginning, the aluminium surface was covered by isolated nanowires. Later, the surface was completely covered by three-dimensional maze-like nanostructure consisting of nanowires. Finally, the nano-sheets, mostly oriented normally to the plate surface with average thickness about 10 nm, formed over the maze structure. The average period of nanostructure monotonously decreased with temperature from 76 to 48 nm. The thickness of nanostructured layer varied between 350 and 550 nm without marked temperature dependence. Hot water treatment allowed achieving the superhydrophilic surface state with contact angle close to zero. The lifetime of this state increased with temperature and achieved hundreds of hours.

The formation of the water suspension of the spherical metal oxide nanoparticles with average sizes ranging from 20 to 40 nm appeared as a result of HWT has been demonstrated. The obtained results allow applying hot water treatment for production of superhydrophilic surfaces covered by nanostructures and aqueous suspensions of nanoparticles of various metal oxides.

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